

Improvements in or relating to Cold-Curing Two-Part Acrylic Resin Compositions and Electric Insulating Materials Embodying them

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Abstract of GB1157436

1,157,436. Cable joints and terminations; repairing cables. BRITISH INSULATED CALLENDER'S CABLES Ltd., and C.M.W. LABORATORIES Ltd. 25 Oct., 1967 [26 Oct., 1966], No. 47979/66. Headings H2C and H2E. [Also in Divisions C3 and H1] Electric cables and joints, repairs or terminations for electric cables comprise at least one insulating body of a synthetic resin made by mixing two syrups A and B and allowing the mixture to cure. Syrup A comprises a solution of a methyl methacrylate polymer in methyl methacrylate monomer containing a polymerization inhibitor and an amine polymerization catalyst promoter, and syrup B comprises one or more plasticizers and a polymerization catalyst. A cable joint or termination may be produced by filling a cavity or enclosure directly or indirectly surrounding a jointed or terminated cable core with the mixture of syrups; the cavity or enclosure may be partly filled with pieces of a solid, non-porous material, e.g. granite chippings (Example VI). Moulded resin bodies can also be obtained by direct polymerization of the syrup mixture. In another embodiment, fibrous structures forming parts of electric cables or joints or terminations therefor are impregnated with the syrup mixture which is then cured; the fibrous structure may be composed of a textile fabric (Examples II-IV).

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PATENT SPECIFICATION

NO DRAWINGS

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COMPLETE SPECIFICATION

Improvements in or relating to Cold-Curing Two-Part Acrylic Resin Compositions and Electric Insulating Materials Embodying them

We, BRITISH INSULATED CABLES LIMITED, of 21, Bloomsbury Street, London, W.C.1, and C.M.W. LABORATORIES LIMITED, of Preston New Road, Blackpool, Lancashire, both British Companies, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to cold-curing two-part synthetic resin compositions that is to say resin compositions of the kind comprising two parts that can be mixed together and then used in a liquid or semi-liquid condition and, after mixing, set to a hard infusible mass without the application of heat. The invention also relates to devices and apparatus and parts thereof encapsulated, filled and/or impregnated with such compositions.

The synthetic resin compositions hitherto in common use for such purposes are the epoxy resins and the polyurethane resins. Both have their disadvantages. The epoxy resin compositions have generally too high a viscosity to ensure completely satisfactory impregnation and require up to 48 hours to set. In addition considerable precautions must be taken by persons handling these compositions to protect themselves from dermatitic hazards arising from these products. The polyurethane resins have a viscosity low enough to permit satisfactory impregnation but are insufficiently able to withstand attack by water. They cannot therefore be relied upon to form encapsulants of electric devices or other articles from which it is essential to exclude moisture or as impregnants of porous articles that are required to be made completely impervious to moisture. Examples of such porous articles are fabric poultices applied to electric cables and cable joints.

The present invention provides an improved two-part cold-curing synthetic resin composition, a method of manufacturing the resin, and improved encapsulated, filled and/or impregnated articles, the improved resin composition being non-toxic and, in the freshly mixed state, having a low viscosity as compared with epoxy resin systems and, in the cured state, being substantially impermeable to water and substantially unaffected by bacterial action and soil acids.

The resin composition in accordance with the invention comprises two syrups 'A' and 'B':

Syrup 'A' is a syrup consisting essentially of a solution of a methyl methacrylate polymer in methyl methacrylate monomer containing a stabilizer which acts as a prepolymerisation inhibitor and sufficient of an amine promotor to promote a catalytic polymerisation reaction of the monomer when a suitable catalyst is added to the syrup. The solution is preferably made by adding a bead polymer and/or copolymer of methyl methacrylate to methyl methacrylate monomer, in proportions such that the proportion of monomeric methyl methacrylate to methyl methacrylate polymer is within the range of 2.5 to 3.5 parts by weight:1 part by weight. The polymeric methyl methacrylate constituent is preferably present wholly as a methyl methacrylate homopolymer but it is possible to use a methyl methacrylate copolymer or a mixture of the homopolymer and the copolymer having substantially the same properties as the homopolymer. To this end, the copolymer or homopolymer/copolymer mixture will preferably not contain or be derived from, ingredients containing more than 10% by weight of monomer other than methyl methacrylate. The quantity of amine promotor added to the syrup will normally be within the range of

[Price 4s. 6d.]

0.25% to 0.5% by weight (based on the weight of the solute) the preferred promotor being dimethyl *para*-toluidine.

5 Syrup 'B' consists essentially of one or more plasticisers, and a polymerisation catalyst, preferably a dispersion of an organic peroxide such as benzoyl peroxide in a plasticiser, and the plasticiser is preferably a phthalate such as dimethyl phthalate.

10 Syrup A preferably comprises up to 100 parts per million, based on the fluid content, of the stabilizer, for example, 2,4-di-methyl-6-*tertiary*-butyl phenol, hydroquinone, or the methyl ether of hydroquinone.

15 To increase the hardness of the finally polymerised system by cross-linking a di-functional monomer may be incorporated in Syrup 'A'. The preferred difunctional monomer is ethylene glycol dimethacrylate but longer chain glycol dimethacrylates such as triethylene glycol dimethacrylate may be used. Alternatively, or in addition, divinyl benzene and/or diethylene glycol diallyl carbonate may be used for this purpose.

25 Other plasticisers preferred for Syrup 'B' are dicyclohexyl phthalate and di-isobutyl phthalate. Syrup 'B' may also contain one or more extenders and the preferred extender is a chlorinated paraffin wax, a typical example of such wax being that sold under the Trade Mark "Cereclor".

30 The invention includes electric cables and joints or terminations for electric cables comprising at least one insulating body of the synthetic resin made by mixing Syrups A and B and allowing the mixture to cure. In one such joint or termination, a cavity or enclosure directly or indirectly surrounding a jointed or terminated cable core or cores is filled with a mixture of Syrups A and B or is first at
40 at least partly filled with pieces of a solid substantially non-porous material that does not react with the resin but to which the resin

adheres when it hardens and then the whole or substantially the whole of the remainder of the space in the cavity or enclosure is filled with the mixture of Syrups A and B. Moulded resin bodies for use in cables, cable joints or terminations can also be made from the resin. The resin compositions formed by mixing the two Syrups are especially suitable as impregnants for fibrous structures forming parts of electric cables or joints or terminations therefor and the invention includes a method of building up such structures by applying fibrous material and either simultaneously or subsequently impregnating it with the Syrup mixture.

For some applications of the improved resin composition it may be necessary for the mixture of Syrups 'A' and 'B' to have a higher initial viscosity. In such cases Syrup 'B' may be thickened by a vinyl chloride/maleic anhydride copolymer or a vinyl acetate/maleic anhydride copolymer. The incorporation of such a copolymer also increases the adhesion of the polymerised system to polyvinyl chloride compositions.

For some purposes it is an advantage to reduce the inflammability of the polymerised resin system and this is preferably done by the addition of non-volatile and non-toxic chlorinated phosphate compounds to Syrup 'B'. An example of such chlorinated phosphate compound is tris(2,3-dichloropropyl)phosphate.

The invention will be further illustrated by a description of Examples of the two-part resin composition and by a description of electric cables, cable joints and cable terminations incorporating the two-part resin.

EXAMPLE I

This is an example of a Syrup 'A' and a compatible Syrup 'B' suitable for making a mixture for use for cable jointing purposes. The composition of the Syrup is as follows:

Syrup 'A'

Methyl methacrylate polymer	30 lbs.
Methyl methacrylate monomer	70 lbs.
2,4-Di-Methyl-6- <i>Tertiary</i> -Butyl Phenol	35 ppm.
D.M.P.T. (dimethyl <i>para</i> toluidine)	0.4 lbs.
Ethylene Glycol Dimethacrylate	1.5 lbs.

Syrup 'B'

Chlorinated paraffin wax	40 lbs.
Dicyclohexyl phthalate	20 lbs.
5% Benzoyl peroxide paste in dimethyl phthalate	2 lbs.

5 Syrups 'A' and 'B' are mixed together in the proportion of 2.3 parts by weight of Syrup 'A' to one part by weight of Syrup 'B' to give a solution of which the viscosity is sufficiently low (being 2 minutes of No. 4 Ford Cup at 1 minute after mixing) to impregnate com-

pletely a poultice of textile fabric and which will self-harden within one hour.

10 In a modification of this example, Syrup 'B' incorporates a flame-proofing agent. The composition of the Syrup is as follows:

Chlorinated paraffin wax	40 parts by weight
Tri tolyl phosphate	30 " " "
Tris(2,3-dichloropropyl) phosphate	10 " " "
Benzoyl peroxide paste (as above)	2 " " "

15 In this modification an additional non-flam agent, namely tri tolyl phosphate is also used. Tri cresyl phosphate could also be used in addition to or instead of the tri tolyl phosphate.

20 Examples of electric cables and cable joints and terminations in which the resin made by mixing together Syrups 'A' and 'B' can be used are as follows:

EXAMPLE II

25 The mixture of Syrups 'A' and 'B' is used as an impregnant for poultices of textile fabrics for use in jointing, terminating and repair of electric cables. Such poultices are preferably built-up *in situ* by applying successive layers of the textile material, which may be made from organic or inorganic fibres, and impreg-
30 nating each layer or each of a number of groups of layers with the syrup mixture as the poultice is built up. Alternatively the textile material can be impregnated with the syrup mixture immediately before application of the textile material or the whole poultice
35 can be built-up dry and then impregnated with the syrup mixture. Such a poultice can for example be used as a seal between a metal or plastics or rubber or synthetic rubber
40 cable sheath and a fitting, for example a gland, through which the cable passes, the poultice being built-up *in situ* after the cable has been inserted through a suitable aperture in the fitting. The fitting may for example be a part
45 of a joint enclosure or a part of a cable termination.

EXAMPLE III.

A similar structure to that described in Example II is built-up over the whole length of a joint enclosure or the enclosure for a
50 termination by applying a lapping of textile fabric to a tubular support surrounding the joint and to the neighbouring part or parts of the cable length or cable lengths and impreg-
55 nating the fabric during or subsequent to its application with a mixture of Syrups A and B. If required an outer envelope of a plastics material resistant to the action of the syrup
60 mixture and to the resin impregnated fabric is subsequently applied overall.

EXAMPLE IV.

A similar structure to that described in Example III is made by applying the whole of the fabric to the enclosure and subsequently
65 impregnating it with the syrup mixture by applying a loose flexible covering to the fabric body to be impregnated, introducing the syrup mixture into the space between the body and the covering and working the mixture into
70 the body by a kneading operation applied to the outside of the flexible covering. With this method of impregnation an outer envelope is preferably applied over the loose flexible
75 covering after completion of the kneading operation but before the resin has set. This technique can be applied to joints or terminations or to cables at positions where a repair is to be effected or a block to the passage of gas or water along the cable is to be created.

EXAMPLE V.

The syrup mixture is used to fill the space between a jointed or terminated core or cores and the joint sleeve or terminal box or that
 5 between a joint sleeve or terminal box and an outer container.

EXAMPLE VI

A modification of Example V in which the space is filled with a mass comprising an aggregate of solid material embedded in a solidified matrix of the resin composition. The
 10 sold material is non-porous and does not react with the synthetic resin composition but the composition adheres to it when it hardens. An
 15 example of such an aggregate material is granite chippings. The space is first at least

partly filled with the granite chippings or other aggregate and the whole or substantially the whole of the remainder of the space is then
 20 filled with the syrup mixture.

EXAMPLE VII

Solid bodies are made from the syrup mixture with or without a fibrous or other filler for use in joint structures and terminations for electric power cables. An example of such
 25 bodies is a moulded test end for mounting on the end of a cable core during high voltage testing.

Specific examples of the structures referred to in Examples II, III, VI and VII are the
 30 subject of the following U.K. Patents and pending Patent Applications—

Example	U.K. Patent or Application Nos.
II	833,787
	870,165
	966,125
III	1,065,431
VI	48855/65 (Serial No. 1157435)
VII	893,376
	930,017

WHAT WE CLAIM IS:—

35 1. A cold-curing two-part resin composition comprising two syrups A and B in which: Syrup 'A' is a syrup consisting essentially of a solution of a methyl methacrylate polymer in methyl methacrylate monomer containing
 40 a stabiliser which acts as a prepolymerisation inhibitor and sufficient of an amine promotor to promote a catalytic polymerisation reaction of the monomer when a suitable catalyst is added to the syrup; and Syrup 'B' consists
 45 essentially of one or more plasticisers and said catalyst.

2. A cold-curing two-part resin composition comprising two syrups A and B in which: Syrup 'A' is a syrup consisting essentially of a
 50 solution of a bead polymer of methyl methacrylate in methyl methacrylate monomer, within the range of 2.5 to 3.5 parts of monomer to one part by weight of bead polymer, a stabiliser which acts as a prepolymerisation
 55 inhibitor, and 0.25 to 0.5% by weight, based on the weight of the solution, of an amine promotor capable of promoting catalytic polymerisation of the composition; and Syrup 'B' consists essentially of one or more plasticisers
 60 and a polymerisation catalyst.

3. A method of manufacturing a cold-curing

two-part resin composition which comprises preparing two syrups 'A' and 'B' as follows: Syrup 'A', a syrup consisting essentially of a methyl methacrylate polymer, methyl methacrylate monomer, a stabiliser which acts as a prepolymerisation inhibitor and an amine
 65 promotor, by dissolving a methyl methacrylate bead polymer, said stabiliser and sufficient of an amine promotor to promote a catalytic polymerisation reaction, when a suitable catalyst is added to the syrup, in methyl methacrylate monomer; and Syrup 'B', a syrup
 70 containing essentially one or more plasticisers and said catalyst, by mixing the plasticiser or plasticisers and the catalyst.

4. A method or composition as claimed in any preceding claim in which the amine promotor is dimethyl *para*-toluidine.

5. A method or composition as claimed in any preceding Claim in which Syrup A is stabilized by up to 100 parts per million, based on the total fluid content, of the stabilizer.

6. A method or composition as claimed in Claim 5 in which the stabilizer is 2,4-dimethyl-6-*tertiary*-butyl phenol, hydroquinone, or the methyl ether of hydroquinone.

7. A method or composition as claimed in

- any preceding Claim in which a di-functional monomer adapted to increase the the hardness of the finally polymerised system is added to Syrup A.
- 5 8. A method or composition as claimed in Claim 7 in which the di-functional monomer is ethylene glycol di-methacrylate.
9. A method or composition as claimed in Claim 7 in which the di-functional monomer is a longer chain glycol dimethacrylate than ethylene glycol dimethacrylate.
- 10 10. A method of composition as claimed in Claim 7 in which the di-functional monomer is divinyl benzene and/or diethylene glycol diallyl carbonate.
- 15 11. A method or composition as claimed in any preceding Claim in which an extender is added to Syrup B.
12. A method or composition as claimed in Claim 11 in which the extender is chlorinated paraffin wax.
- 20 13. A method or composition as claimed in any preceding Claim in which Syrup B is thickened by the addition of a vinyl chloride/maleic anhydride copolymer or a vinyl acetate/maleic anhydride copolymer.
- 25 14. A method or composition as claimed in any preceding Claim in which Syrup B contains a non-volatile and non-toxic chlorinated phosphate compound in order to reduce the inflammability of the resin system when cured.
- 30 15. A method or composition as claimed in any preceding Claim in which the catalyst is an organic peroxide.
- 35 16. A method or composition as claimed in Claim 15 in which the catalyst is benzoyl peroxide.
17. A method or composition as claimed in any preceding Claim in which the plasticiser is a phthalate.
- 40 18. A method as claimed in Claim 17 in which the plasticiser is dimethyl, dicyclohexyl or di-isobutyl phthalate.
19. A method or composition as claimed in any preceding Claim in which Syrup B is of a composition substantially as hereinbefore described with reference to the modification of Example I.
- 45 20. A cold-curing two-part resin composition substantially as hereinbefore described in Example I.
21. A method of making a synthetic resin body which comprises mixing a Syrup A and a Syrup B as defined in any preceding Claim and allowing the mixture to cure.
- 50 22. A synthetic resin body made by the method claimed in Claim 21.
23. An electric cable structure or a joint or termination for an electric cable comprising at least one insulating synthetic resin body in which the resin is made by mixing two Syrups A and B in which: Syrup 'A' is a syrup consisting essentially of a solution of a methyl methacrylate polymer in methyl methacrylate monomer containing a stabiliser which acts as
- 55 65 a prepolymerisation inhibitor and sufficient of an amine promotor to promote a catalytic polymerisation reaction when a suitable catalyst is added to the syrup; and Syrup 'B' consists essentially of one or more plasticisers and said catalyst.
- 70 24. A joint or termination as claimed in Claim 23 in which the resin is made by mixing Syrups A and B as defined in any of Claims 2 and 4—19.
- 75 25. A method of making a joint or termination for an electric cable comprising a cavity or an enclosure directly or indirectly surrounding a jointed or terminated cable core or cores which comprises filling said cavity or enclosure with a cold-curing resin composition made by mixing two Syrups A and B in which: Syrup 'A' is a syrup consisting essentially of a solution of a methyl methacrylate polymer in methyl methacrylate monomer containing a stabiliser which acts as a prepolymerisation inhibitor and sufficient of an amine promotor to promote a catalytic polymerisation reaction when a suitable catalyst is added to the syrup; and Syrup 'B' consists essentially of one or more plasticisers and said catalyst.
- 80 26. A method as claimed in Claim 25 in which the enclosure or cavity is at least partly filled with pieces of a solid, substantially non-porous material that does not react with the resin but to which the resin adheres when it hardens and the whole or substantially the whole of the remainder of the space in the cavity or enclosure is then filled with the mixture of the syrups.
- 85 27. A method as claimed in Claim 25 or 26 in which the resin composition is made by mixing Syrups A and B as defined in any of Claims 2 and 4—19.
- 90 28. An electric cable structure or a joint or termination for an electric cable comprising at least one insulating body formed by impregnating a fibrous structure with a cold-curing resin composition made by mixing two syrups A and B in which: Syrup 'A' is a syrup consisting essentially of a solution of a methyl methacrylate polymer in methyl methacrylate monomer containing a stabiliser which acts as a prepolymerisation inhibitor and sufficient of an amine promotor to promote a catalytic polymerisation reaction when a suitable catalyst is added to the syrup; and Syrup 'B' consists essentially of one or more plasticisers and said catalyst.
- 95 29. An electric cable or cable joint or termination as claimed in Claim 28 in which the resin composition is made by mixing Syrups A and B as defined in any of Claims 2 and 4—19.
- 100 30. An electric cable or cable joint or termination substantially as hereinbefore described in any one of examples II—VII and incorporating a resin composition as claimed in any one of claims 1, 2 and 4—20.
- 105 110 115 120 125 130

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